

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 October 2003 (09.10.2003)

PCT

(10) International Publication Number
WO 03/082930 A2

- (51) International Patent Classification⁷: **C08F 4/00**
- (21) International Application Number: **PCT/EP03/02819**
- (22) International Filing Date: **17 March 2003 (17.03.2003)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
02076256.3 **29 March 2002 (29.03.2002)** **EP**
- (71) Applicant (for all designated States except US): **BASELL POLIOLEFINE ITALIA S.P.A. [IT/IT]; Via Pergolesi, 75, I-20124 Milano (IT).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **EVANGELISTI, Daniele [IT/IT]; Via del Campo, 28, I-44100 Ferrara (IT). COLLINA, Gianni [IT/IT]; Via XXI Aprile 1945, 3, I-44044 Cassana-Ferrara (IT).**
- (74) Agent: **COLUCCI, Giuseppe; Basell Poliolefine Italia S.P.A, Intellectual Property, P.le G. Donegani 12, I-44100 Ferrara (IT).**
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**
- Declaration under Rule 4.17:**
— *of inventorship (Rule 4.17(iv)) for US only*
- Published:**
— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 03/082930 A2

(54) Title: **MAGNESIUM DICHLORIDE-ETHANOL ADDUCTS AND CATALYST COMPONENTS OBTAINED THEREFROM**

(57) Abstract: The present invention relates to a $\text{MgCl}_2 \cdot m\text{EtOH}$ adduct in which m is from 2.5 to 3.2 optionally containing water up to a maximum of 1%wt based on the total weight of the adduct, characterized by a DSC profile in which the highest melting Temperature (T_m) peak is over 109°C and has an associated fusion enthalpy (ΔH) of 103 J/g or lower. Catalyst components obtained from the adducts of the present invention are capable to give catalysts for the polymerization of olefins characterized by enhanced activity with respect to the catalysts prepared from the adducts of the prior art.

"Magnesium dichloride-ethanol adducts and catalyst components obtained therefrom"

The present invention relates to magnesium dichloride/ethanol adducts which are characterized by particular chemical and physical properties. The adducts of the present invention are particularly useful as precursors of catalyst components for the polymerization of olefins.

MgCl₂•alcohol adducts and their use in the preparation of catalyst components for the polymerization of olefins are well known in the art. Catalyst components for the polymerization of olefins, obtained by reacting MgCl₂•nEtOH adducts with halogenated transition metal compounds, are described in USP 4,399,054. The adducts are prepared by emulsifying the molten adduct in an immiscible dispersing medium and quenching the emulsion in a cooling fluid to collect the adduct in the form of spherical particles. No physical characterization regarding the degree of crystallinity of the adducts are reported.

In WO98/44009 are disclosed MgCl₂•alcohol adducts having improved characteristics and characterized by a particular X-ray diffraction spectrum, in which, in the range of 2θ diffraction angles between 5° and 15°, the three main diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction lines being the one at $2\theta=8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line. Said adducts can be of formula MgCl₂•mEtOH•nH₂O

where m is between 2.2 and 3.8 and n is between 0.01 and 0.6. In addition to the above described X-ray spectrum, the above described adducts are characterized by a Differential Scanning Calorimetry (DSC) profile in which no peaks are present at temperatures below 90°C or, even if peaks are present below said temperature, the fusion enthalpy associated with said peaks is less than 30% of the total fusion enthalpy. The adducts prepared according to the procedures reported in the working examples have always DSC profiles such that the peak at highest temperature does not reach 109°C and namely falls within the 100-108°C range.

These adducts are obtained by specific preparation methods involving the reaction between MgCl₂ and alcohol under conditions such long reaction times and absence of inert diluents or use of vaporized alcohol. Nothing is said, in the working examples, about the water content. The catalyst components obtained from these adducts have an increased activity over those obtained from the adducts of the prior art. However, the availability of catalyst components with still improved activity is always needed in view of the economic advantages obtainable in the operation of the industrial plants.

The applicant has now found new MgCl₂•mEtOH adducts having specific chemical and physical

properties. The adducts of the present invention can be used to prepare catalyst components for the polymerization of olefins by reacting them with transition metal compounds. Catalyst components obtained from the adducts of the present invention are capable to give catalysts for the polymerization of olefins characterized by enhanced activity with respect to the catalysts prepared from the adducts of the prior art.

The present invention therefore relates to $\text{MgCl}_2 \cdot m\text{EtOH}$ adducts in which m is from 2.5 to 3.2 optionally containing water up to a maximum of 1%wt based on the total weight of the adduct, characterized by a DSC diagram (profile) in which the highest melting Temperature (T_m) peak is over 109°C and has an associated fusion enthalpy (ΔH) of 103J/g or lower.

Preferably, the water content is lower than 0.8% wt and preferably lower than 0.6%wt. In a particular aspect, the highest melting Temperature (T_m) peak is over 110°C and more preferably over 111°C . Preferably, the fusion enthalpy associated to it is lower than 102 J/g and most preferably in the range 97-101 J/g.

Particularly interesting are the adducts showing, in the DSC diagram (profile), only one peak, however, additional peaks in the $95\text{-}98^\circ\text{C}$ region may be present. In the latter case however, the fusion enthalpy associated to them is lower than 30% of the total fusion enthalpy, preferably lower than 20 and more preferably lower than 10%. The DSC analysis is carried out using the apparatus and the methodology described hereinafter.

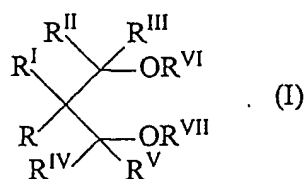
It is possible, but not strictly required, that also the adduct of the present invention are characterized by an X-ray diffraction spectrum in which, in the range of 2θ diffraction angles between 5° and 15° , the three main diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction lines being the one at $2\theta = 8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line.

The adducts of the present invention can be prepared according to several methods. In particular the general methods described in WO98/44009 are suitable with the proviso that the amount of water is carefully controlled. A particular attention should be paid to the water content of the reactants. Both MgCl_2 and EtOH are in fact highly hygroscopic and tend to incorporate water in their structure. As a result, if the water content of the reactants is relatively high, the final MgCl_2 -EtOH adducts may contain a too high water content even if water has not been added as a separate component. Means for controlling or lowering the water content in solids or fluids are well known in the art. The water content in MgCl_2 can be for example lowered by drying it in an oven at high

temperatures or by reacting it with a compound which is reactive towards water. As an example, a stream of HCl can be used to remove water from MgCl_2 . Water from the fluids can be removed by various techniques such as distillation or by allowing the fluids to become in contact with substances capable to subtract water such as molecular sieves. Once this precautions have been taken, the reaction between the magnesium chloride and ethanol to produce the adducts of the invention can be carried out according to various methods. According to one of these methods the adducts are prepared by dispersing the particles of magnesium dichloride in an inert liquid immiscible with and chemically inert to the molten adduct, heating the system at temperature equal to or higher than the melting temperature of MgCl_2 -ethanol adduct and then adding the desired amount of alcohol in vapour phase. The temperature is kept at values such that the adduct is completely melted.

The molten adduct is then emulsified in a liquid medium which is immiscible with and chemically inert to it and then quenched by contacting the adduct with an inert cooling liquid, thereby obtaining the solidification of the adduct. The liquid in which the MgCl_2 is dispersed can be any liquid immiscible with and chemically inert to the molten adduct. For example, aliphatic, aromatic or cycloaliphatic hydrocarbons can be used as well as silicone oils. Aliphatic hydrocarbons such as vaseline oil are particularly preferred. After the MgCl_2 particles are dispersed in the inert liquid, the mixture is heated at temperatures preferably higher than 125°C and more preferably at temperatures higher than 150°C . Conveniently, the vaporized alcohol is added at a temperature equal to or lower than the temperature of the mixture. According to another method, the adducts of the invention are prepared by contacting MgCl_2 and alcohol in the absence of the inert liquid dispersant, heating the system at the melting temperature of MgCl_2 -alcohol adduct or above, and maintaining said conditions so as to obtain a completely melted adduct. Said molten adduct is then emulsified in a liquid medium which is immiscible with and chemically inert to it and finally quenched by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct. In particular, the adduct is preferably kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period equal to or greater than 10 hours, preferably from 10 to 150 hours, more preferably from 20 to 100 hours. Alternatively, in order to obtain the solidification of the adduct, a spray-cooling process of the molten adduct can be carried out. All these methods provide solid adducts having a spherical morphology which are very suitable in the preparation of spherical catalyst components for the polymerization of olefins and in particular for the gas-phase polymerization process.

The said catalyst components to be used in the polymerization of olefins can be obtained by a reacting the adducts of the invention and a transition metal compound of one of the groups 4-6 of the Periodic Table of Elements (new notation). Among transition metal compounds particularly preferred are titanium compounds of formula $Ti(OR)_nX_{y-n}$ in which n is comprised between 0 and y ; y is the valence of titanium; X is halogen and R is an alkyl radical having 1-8 carbon atoms or a COR group. Among them, particularly preferred are titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates. Preferred specific titanium compounds are $TiCl_3$, $TiCl_4$, $Ti(OBu)_4$, $Ti(OBu)Cl_3$, $Ti(OBu)_2Cl_2$, $Ti(OBu)_3Cl$. Preferably the reaction is carried out by suspending the adduct in cold $TiCl_4$ (generally $0^\circ C$); then the so obtained mixture is heated up to $80-130^\circ C$ and kept at this temperature for 0.5-2 hours. After that the excess of $TiCl_4$ is removed and the solid component is recovered. The treatment with $TiCl_4$ can be carried out one or more times. The reaction between transition metal compound and the adduct can also be carried out in the presence of an electron donor compound (internal donor) in particular when the preparation of a stereospecific catalyst for the polymerization of olefins is to be prepared. Said electron donor compound can be selected from esters, ethers, amines, silanes and ketones. As a result of this contact the electron donor compound remains deposited on the catalyst component. In particular, the alkyl and aryl esters of mono or polycarboxylic acids such as for example esters of benzoic, phthalic, malonic and succinic acid are preferred. Specific examples of such esters are *n*-butylphthalate, di-isobutylphthalate, di-*n*-octylphthalate, diethyl 2,2-diisopropylsuccinate, diethyl 2,2-dicyclohexyl-succinate, ethyl-benzoate and *p*-ethoxy ethyl-benzoate. Moreover, can be advantageously used also the 1,3 diethers of the formula:



wherein R , R^I , R^{II} , R^{III} , R^{IV} and R^V equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VI} and R^{VII} , equal or different from each other, have the same meaning of $R-R^V$ except that they cannot be hydrogen; one or more of the $R-R^{VII}$ groups can be linked to form a cycle. The 1,3-diethers in which R^{VI} and R^{VII} are selected from C_1 - C_4 alkyl radicals are particularly preferred.

The electron donor compound is generally present in molar ratio with respect to the magnesium

comprised between 1:4 and 1:20.

Preferably, the particles of the solid catalyst components have substantially spherical morphology and an average diameter comprised between 5 and 150 μm . With the term substantial spherical morphology are meant those particles having a ratio between the greater and smaller axis equal to or lower than 1.5 and preferably lower than 1.3.

Before the reaction with the transition metal compound, the adducts of the present invention can also be subjected to a dealcoholation treatment aimed at lowering the alcohol content and increasing the porosity of the adduct itself. The dealcoholation can be carried out according to known methodologies such as those described in EP-A-395083. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 2.6 moles of alcohol per mole of MgCl_2 . After the dealcoholation treatment the adducts are reacted with the transition metal compound, according to the techniques described above, in order to obtain the solid catalyst components.

The solid catalyst components according to the present invention show a surface area (by B.E.T. method) generally between 10 and 500 m^2/g and preferably between 20 and 350 m^2/g , and a total porosity (by B.E.T. method) higher than 0.15 cm^3/g preferably between 0.2 and 0.6 cm^3/g . Surprisingly, the catalyst components comprising the reaction product of a transition metal compound with a MgCl_2 -alcohol adduct which is in turn obtained by partially dealcoholating the adducts of the invention, show improved properties, particularly in terms of activity, with respect to the catalyst components prepared from the dealcoholated adducts of the prior art. The catalyst components of the invention form catalysts for the polymerization of alpha-olefins $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, by reaction with Al-alkyl compounds. The alkyl-Al compound is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$ optionally in mixture with said trialkyl aluminum compounds..

The Al/Ti ratio is higher than 1 and is generally comprised between 20 and 800.

In the case of the stereoregular polymerization of α -olefins such as for example propylene and 1-butene, an electron donor compound (external donor) which can be the same or different from the compound used as internal donor can be used in the preparation of the catalysts disclosed above. In case the internal donor is an ester of a polycarboxylic acid, in particular a phthalate, the external

donor is preferably selected from the silane compounds containing at least a Si-OR link, having the formula $R_a^1R_b^2Si(OR^3)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1 , R^2 , and R^3 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^1 and R^2 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R^3 is a C_1 - C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R^2 is a branched alkyl or cycloalkyl group and R^3 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.

Also the 1,3 diethers having the previously described formula can be used as external donor. However, in the case 1,3-diethers are used as internal donors, the use of an external donor can be avoided, as the stereospecificity of the catalyst is already sufficiently high.

As previously indicated the components of the invention and catalysts obtained therefrom find applications in the processes for the (co)polymerization of olefins of formula $CH_2=CHR$ in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms.

The catalysts of the invention can be used in any of the olefin polymerization processes known in the art. They can be used for example in slurry polymerization using as diluent an inert hydrocarbon solvent or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, they can also be used in the polymerization process carried out in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.1 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa.

The catalysts of the invention are very useful for preparing a broad range of polyolefin products. Specific examples of the olefinic polymers which can be prepared are: high density ethylene polymers (HDPE, having a density higher than 0.940 g/cc), comprising ethylene homopolymers and copolymers of ethylene with alpha-olefins having 3-12 carbon atoms; linear low density polyethylenes (LLDPE, having a density lower than 0.940 g/cc) and very low density and ultra low density (VLDPE and ULDPE, having a density lower than 0.920 g/cc, to 0.880 g/cc) consisting of

copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms, having a mole content of units derived from the ethylene higher than 80%; isotactic polypropylenes and crystalline copolymers of propylene and ethylene and/or other alpha-olefins having a content of units derived from propylene higher than 85% by weight; copolymers of propylene and 1-butene having a content of units derived from 1-butene comprised between 1 and 40% by weight; heterophasic copolymers comprising a crystalline polypropylene matrix and an amorphous phase comprising copolymers of propylene with ethylene and or other alpha-olefins.

The following examples are given to illustrate and not to limit the invention itself.

CHARACTERIZATION

The properties reported below have been determined according to the following methods:

The DSC measurement were carried out with a METTLER DSC 30 instrument at a scanning rate of 5°C/min in the range 5-125°C. Aluminum capsules having a volume of 40µl filled with the samples in a dry-box were used in order to avoid hydration of the samples.

EXAMPLES

General procedure for the preparation of the catalyst component

Into a 1l steel reactor provided with stirrer, 800cm³ of TiCl₄ at 0°C were introduced; at room temperature and whilst stirring 16 g of the adduct were introduced together with an amount of diisobutylphthalate as internal donor so as to give a donor/Mg molar ratio of 10. The whole was heated to 100°C over 90 minutes and these conditions were maintained over 120 minutes. The stirring was stopped and after 30 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 100°C. A further treatment of the solid was carried out adding 750 cm³ of TiCl₄ and heating the mixture at 120°C over 10 min. and maintaining said conditions for 60 min under stirring conditions (500 rpm). The stirring was then discontinued and after 30 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 120°C. Thereafter, 3 washings with 500 cm³ of anhydrous hexane at 60°C and 3 washings with 500 cm³ of anhydrous hexane at room temperature were carried out. The solid catalyst component obtained was then dried under vacuum in nitrogen environment at a temperature ranging from 40-45°C.

General procedure for the polymerization test

A 4 litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst feeding system, monomer feeding lines and thermostating jacket, was used. The reactor was charged with 0.01 gr. of solid catalyst component 0,76 g of TEAL, 0.076g of dicyclopentyl dimethoxy silane, 3.2 l

of propylene, and 1.5 l of hydrogen. The system was heated to 70°C over 10 min. under stirring, and maintained under these conditions for 120 min. At the end of the polymerization, the polymer was recovered by removing any unreacted monomers and was dried under vacuum.

EXAMPLE 1

In a vessel reactor equipped with a IKA RE 166 stirrer containing 115,3 g of anhydrous EtOH at room temperature were introduced under stirring 81.7 gr. of MgCl_2 containing 0.3% water. Once the addition of MgCl_2 was completed, the temperature was raised up to 125°C and kept at this value for 3 hours. After that, 1600 cm^3 of OB55 vaseline oil were introduced and, while keeping the temperature at 125°C, the stirring was brought to 1500 rpm and kept at that value for two minutes. After that time the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C. After 12 hours, the solid particles of the $\text{MgCl}_2 \bullet \text{EtOH}$ adduct recovered were then washed with hexane and dried at 40°C under vacuum. The compositional analysis showed that they contained 57.7 % by weight of EtOH and 0.3% of water.

The DSC profile showed a peak at 112.3°C, with an associated fusion enthalpy of 97.75 J/g. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

EXAMPLE 2

In a vessel reactor equipped with a IKA RE 166 stirrer containing 139.16g of anhydrous EtOH at room temperature were introduced under stirring 94.64g of MgCl_2 containing 0.3% water. Once the addition of MgCl_2 was completed the temperature was raised up to 125°C and kept at this value for 3 hours. After that, 1550 cm^3 of OB55 vaseline oil were introduced and, while keeping the temperature at 125°C, the stirring was brought to 1500 rpm and kept at that value for two minutes. After that time the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C. After 12 hours, the solid particles of the $\text{MgCl}_2 \bullet \text{EtOH}$ adduct recovered were then washed with hexane and dried at 40°C under vacuum. The solid particles of the $\text{MgCl}_2 \bullet \text{EtOH}$ adduct recovered were then washed with hexane and dried at 40°C under vacuum. The compositional analysis showed that they contained 59.2 % by weight of EtOH and 0.65% of water.

The DSC profile showed a peak at 110.1°C, with an associated fusion enthalpy of 98.7 J/g. and a peak at 93.3°C, with an associated fusion enthalpy of 20.6 J/g. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure

described above and gave the results reported in Table 1.

COMPARISON EXAMPLE 1

The procedure of Example 1 was repeated with the difference that the 115.3 g of ethanol were added with 2.95 g of water. The compositional analysis showed that they contained 57.6 % by weight of EtOH and 1.65% of water. The DSC profile showed a peak at 105.6°C, with an associated fusion enthalpy of 97.6 J/g and a peak at 76°C °C, with an associated fusion enthalpy of 21.6 J/g. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

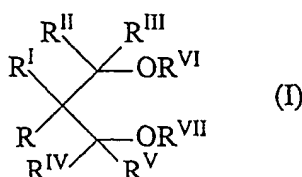
TABLE 1

Example	Activity	II:	Poured bulk density
1	78	98.3	0.48
2	81	98.5	0.45
Comp.1	70	98.2	0.46

CLAIMS

1. A $\text{MgCl}_2 \cdot m\text{EtOH}$ adduct in which m is from 2.5 to 3.2 characterized by a DSC diagram in which the highest melting Temperature (T_m) peak is over 109°C and has an associated fusion enthalpy (ΔH) of 103J/g or lower.
2. The adduct according to claim 1 containing water up to 1%wt based on the total weight of the adduct.
3. The adduct according to claim 2 in which the water content is lower than 0.8% wt.
4. The adduct according to claim 3 in which the water content is lower than 0.6%wt.
5. The adduct according to claim 1 in which the highest melting Temperature (T_m) peak is over 110°C .
6. The adduct according to claim 5 in which the highest melting Temperature (T_m) peak is over 111°C .
7. The adduct according to claim 1 in which the fusion enthalpy associated to the highest melting Temperature (T_m) peak is lower than 102 J/g .
8. The adduct according to claim 7 in which the fusion enthalpy associated to the highest melting Temperature (T_m) peak is in the range $97\text{-}101\text{ J/g}$.
9. The adduct according to anyone of the preceding claims further characterized by an X-ray diffraction spectrum in which, in the range of 2θ diffraction angles between 5° and 15° , three main diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction lines being the one at $2\theta = 8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line.
10. The adduct according to claim 1 in form of spheroidal particles .
11. The catalyst component for the polymerization of olefins comprising the product obtained by reacting a transition metal compound of groups IV to VI of the Periodic Table of Elements with an adduct according to anyone of the preceding claims.
12. The catalyst component according to claim 11 in which the transition metal is selected from titanium compounds of formula $\text{Ti}(\text{OR})_n\text{X}_{y-n}$ in which n is comprised between 0 and y ; y is the valence of titanium; X is halogen and R is an alkyl radical having 1-8 carbon atoms or a COR group.
13. The catalyst component according to claim 12 in which the titanium compound is selected from TiCl_3 , TiCl_4 , $\text{Ti}(\text{OBu})_4$, $\text{Ti}(\text{OBu})\text{Cl}_3$, $\text{Ti}(\text{OBu})_2\text{Cl}_2$, $\text{Ti}(\text{OBu})_3\text{Cl}$.

14. The catalyst component according to claim 11 which further contains an electron donor compound.
15. The catalyst component according to claim 14 in which the electron donor is selected from the alkyl or aryl esters of mono or polycarboxylic acids.
16. The catalyst component according to claim 14 in which the electron donor is selected from 1,3 diethers of the formula:



wherein R, R^I, R^{II}, R^{III}, R^{IV} and R^V equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VI} and R^{VII}, equal or different from each other, have the same meaning of R-R^V except that they cannot be hydrogen; one or more of the R-R^{VII} groups can be linked to form a cycle.

17. The catalyst component for the polymerization of olefins according to claim 11 characterized by the fact that before being reacted with the transition metal compound, the adduct is subject to a dealcoholation treatment.
18. The catalyst component for the polymerization of olefins according to claim 18 in which the partially dealcoholated adduct contains from 0.1 to 2.6 moles of alcohol per mole of MgCl₂.
19. Catalyst for the polymerization of olefins comprising the product obtained by contacting a catalyst component according to one of the claims 11 to 18, and an aluminum alkyl compound.
20. The catalyst for the polymerization of olefins according to claim 19 in which the aluminum compound is an Al-trialkyl compound.
21. The catalyst for the polymerization of olefins according to claim 20 further comprising an external donor.
22. The catalyst for the polymerization of olefins according to claim 21 in which the external donor is selected from the silane compounds containing at least a Si-OR link, having the formula R_a¹R_b²Si(OR³)_c, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R¹, R², and R³, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms.
23. Process for the polymerization of olefins of formula CH₂=CHR, in which R is hydrogen or a

hydrocarbon radical having 1-12 carbon atoms, carried out in the presence of a catalyst according to one of the claims 19-22.